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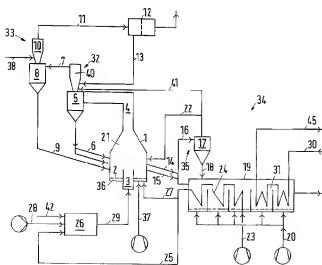
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(54) Title: METHOD AND APPARATUS FOR HEAT TREATMENT IN A FLUIDIZED BED



(57) Abstract: The present invention relates to a method for the heat treatment of fine-grained solids, in particular gypsum, in which the solids are heated to a temperature of 50 to 1000 °C in a fluidized bed reactor (1), and to a corresponding plant. To improve the energy utilization, it is proposed to introduce a first gas or gas mixture from below through a preferably central gas supply tube (3) into a mixing chamber (21) of the reactor (1), the gas supply tube (3) being at least partly surrounded by a stationary annular fluidized bed (2) which is fluidized by supplying fluidizing gas, and to adjust the gas velocities of the first gas or gas mixture as well as of the fluidizing gas for the annular fluidized bed (2) such that the particle Froude numbers in the gas supply tube (3) are between 1 and 100, in the annular fluidized bed (2) between 0.02 and 2 and in the mixing chamber (21) between 0.3 and 30.

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METHOD AND APPARATUS FOR HEAT TREATMENT IN A FLUIDISED BED

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Technical Field

The present invention relates to a method for the heat treatment of fine-grained solids, in particular gypsum, in which the solids are heated to a temperature of 50 to 1000 °C in a fluidized bed reactor, and to a corresponding plant.

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Such methods and plants are used for instance in the calcining of gypsum to form water-free anhydrite. Previously, venturi fluidized beds or fluidized beds with a ceramic perforated bottom were used for this as air distributors. However, this only allowed a small regulating range. In part-load operation or when shutting down the plant, there is also the risk that, in spite of the sophisticated mechanical feature of the perforated bottom, the fine-grained solids fall through the grating.

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Reactors with either a stationary fluidized bed or a circulating fluidized bed are generally known for the heat treatment of solids. However, the energy utilization of the calcining step achieved when using a stationary fluidized bed is in need of improvement. A particular reason for this is that the mass and heat transfer is rather moderate on account of the comparatively low degree of fluidization. Furthermore, pre-heating of the solids can hardly be integrated in a suspension heat exchanger, because dust-laden gases are rather not admitted to the fluidizing nozzles of the stationary fluidized bed. Due to the high degree of fluidization, circulating fluidized beds on the other hand have better conditions for a mass and heat transfer and allow the integration of a suspension heat exchanger, but are restricted in terms of their solids retention time due to the high degree of fluidization.

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Description of the Invention

Therefore, it is the object of the present invention to improve the heat and mass
5 transfer conditions in the heat treatment of fine-grained solids.

In accordance with the invention, this object is achieved by a method as initially
mentioned in which a first gas or gas mixture is introduced from below through a
preferably centrally arranged gas supply tube (central tube) into a mixing cham-
10 ber of the reactor, the central tube being at least partly surrounded by a station-
ary annular fluidized bed which is fluidized by supplying fluidizing gas, and in
which the gas velocities of the first gas or gas mixture as well as of the fluidizing
gas for the annular fluidized bed are adjusted such that the particle Froude
numbers in the central tube are between 1 and 100, in the annular fluidized bed
15 between 0.02 and 2 and in the mixing chamber between 0.3 and 30.

In the method of the invention, the advantages of a stationary fluidized bed,
such as a sufficiently long solids retention time, and the advantages of a circular
fluidized bed, such as a good mass and heat transfer, can surprisingly be com-
20 bined with each other during the heat treatment, while the disadvantages of both
systems are avoided. When passing through the upper region of the central tu-
be, the first gas or gas mixture entrains solids from the annular stationary fluidi-
zied bed, which is referred to as the annular fluidized bed, into the mixing cham-
ber, so that, due to the high slip velocities between the solids and the first gas,
25 an intensively mixed suspension is formed and an optimum heat and mass
transfer between the two phases is achieved. By correspondingly adjusting the
bed height in the annular fluidized bed as well as the gas velocities of the first
gas or gas mixture and of the fluidizing gas, the solids load of the suspension
above the orifice region of the central tube can be varied within wide ranges, so
30 that the pressure loss of the first gas between the orifice region of the central

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tube and the upper outlet of the mixing chamber can be between 1 mbar and 100 mbar. In the case of high solids loading of the suspension in the mixing chamber, a large part of the solids will separate out from the suspension and fall back into the annular fluidized bed. This recirculation is called internal solids
5 recirculation, the stream of solids circulating in this internal circulation normally being significantly larger than the amount of solids supplied to the reactor from outside. The (smaller) amount of not precipitated solids is discharged from the mixing chamber together with the first gas or gas mixture. The retention time of the solids in the reactor can be varied within a wide range by the selection of the
10 height and cross-sectional area of the annular fluidized bed and be adapted to the desired heat treatment. Due to the high solids loading on the one hand and the good suspension of the solids in the gas stream on the other hand, excellent conditions for good mass and heat transfer are obtained above the orifice region of the central tube. The amount of solids entrained from the reactor with the gas
15 stream is completely or at least partly recirculated to the reactor, with the recirculation expediently being fed into the stationary fluidized bed. The stream of solids thus recirculated to the annular fluidized bed normally lies in the same order of magnitude as the stream of solids supplied to the reactor from outside. Apart from the excellent utilization of energy, another advantage of the method
20 in accordance with the invention consists in the possibility of quickly, easily and reliably adjusting the transfer of energy of the method and the mass transfer to the requirements by changing the flow velocities of the first gas or gas mixture and of the fluidizing gas.

25 To ensure a particularly effective heat transfer in the mixing chamber and a sufficient retention time in the reactor, the gas velocities of the first gas mixture and of the fluidizing gas are preferably adjusted for the fluidized bed such that the dimensionless particle Froude numbers (Fr_p) are 1.15 to 20 in the central tube, 0.115 to 1.15 in the annular fluidized bed and/or 0.37 to 3.7 in the mixing chamber. The particle Froude numbers are each defined by the following equation:

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$$Fr_p = \frac{u}{\sqrt{\frac{(\rho_s - \rho_f) * d_p * g}{\rho_f}}}$$

with

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- u = effective velocity of the gas flow in m/s
- ρ_s = density of a solid particle in kg/m³
- ρ_f = effective density of the fluidizing gas in kg/m³
- d_p = mean diameter in m of the particles of the reactor inventory (or the
- 10 particles forming) during operation of the reactor
- g = gravitational constant in m/s².

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When using this equation it should be considered that d_p does not indicate the mean diameter (d₅₀) of the material used, but the mean diameter of the reactor inventory formed during the operation of the reactor, which can differ significantly in both directions from the mean diameter of the material used (primary particles). It is also possible for particles (secondary particles) with a mean diameter of 20 to 30 μm to be formed for instance during the heat treatment from very fine-grained material with a mean diameter of, for example, 3 to 10 μm. On the

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other hand, some materials, for example ores, are decrepitated during the heat treatment.

In a development of the idea of the invention, it is proposed to adjust the bed height of solids in the reactor such that the annular fluidized bed at least partly extends for example beyond the upper orifice end of the central tube by a few

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centimetres, and thus solids are constantly introduced into the first gas or gas mixture and entrained by the gas stream to the mixing chamber located above

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the orifice region of the central tube. In this way, there is achieved a particularly high solids loading of the suspension above the orifice region of the central tube.

With the method in accordance with the invention, in particular moist gypsum, such as for example REA gypsum, can be subjected to effective heat treatment, in order in particular to obtain anhydrous forms of gypsum. The method is particularly suited for producing anhydrite by calcining. The moist gypsum used has in this case a fine granulation, the grain size of at least the majority of the solids generally being less than 2 mm. A particularly effective heat treatment can be achieved in the case of a grain size of less than 0.2 mm. Further application possibilities for the method lie in the pre-heating and/or calcining of ores and mineral raw materials in an oxidizing atmosphere at temperatures up to a maximum of approximately 1000°C, if internal combustion is ruled out, and in the calcining of clay minerals at about 800°C. At temperatures up to about 750°C, the method in accordance with the invention can also be used for producing transitional hydrates or oxides from aluminium hydroxide.

The generation of the amount of heat necessary for the operation of the reactor can be effected in any way known to the expert for this purpose, for example including by internal combustion in the reactor. To be able to use the method in accordance with the invention also for pre-heating and calcining at temperatures of for example approximately 750°C, at which an internal combustion of fuel in the reactor itself is not possible, the invention proposes the use of an external combustion chamber for generating the necessary process heat and a heat transfer to the material (for example gypsum) to be treated in the reactor with the annular fluidized bed. For this purpose, the reactor is supplied via the central tube with hot gas, which is generated in the upstream combustion chamber by burning supplied gaseous, liquid and/or solid fuel, possibly with the admixture of gas containing oxygen. Depending on the necessary oxygen content, air or some other oxygen-containing gas, for example with an oxygen content of 15 to

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30%, may be admixed. Of course it is also possible to generate only part of the energy demand by burning fresh fuel and to cover the remaining part by supplying hot, fuel-free exhaust gases from a downstream stage of the process, for example cooling, or other parallel processes. If the temperatures of the exhaust
5 gases from downstream or parallel stages of the process are adequately high, just these exhaust gases can also be used for heating the reactor. This is possible in particular whenever only low reactor temperatures are required, for example for drying. In this case, it is also possible to dispense entirely with internal combustion or an upstream combustion chamber.

10 Depending on the process taking place in the reactor, the process temperature may lie between 50 and 1000°C. In the lower temperature range from 50°C, in particular from approximately 80°C, the annular fluidized bed reactor may also be used only for drying material. In this case, the temperatures must not exceed
15 an upper limit value, from which the heat-treated material undergoes a chemical reaction. In a common form of the method, a temperature range between 150 and 1000°C is used, for example in the case of calcining.

20 Air is preferably supplied to the reactor as the gas for fluidizing the annular fluidized bed, it of course also being possible for all other gases or gas mixtures known for this purpose to an expert to be used for this purpose. It may also be advantageous to compress dedusted and/or cooled exhaust gas from downstream stages of the process or other parallel processes such that it can be used as fluidizing gas for the annular fluidized bed.

25 It has turned out to be advantageous to operate the reactor at a pressure of 0.8 to 10 bar and particularly preferably at atmospheric pressure.

30 The reactor may be provided upstream with one or more pre-heating stages, in which the solids, for example the moist gypsum, are suspended, dried, pre-

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heated and/or partly calcined in a pre-heating stage before the heat treatment in the reactor, at least part of the moisture content of the solids being removed. The reactor is preferably provided upstream with two pre-heating stages, respectively comprising a heat exchanger and a downstream separator, the material in the first heat exchanger being heated up by exhaust gas from the second heat exchanger and the material in the second heat exchanger being heated up by exhaust gas from the reactor. Both heat exchangers are preferably suspension heat exchangers. In this way, the overall energy demand of the process is further reduced.

In accordance with the method according to the invention, after the heat treatment in the reactor, the product from the annular fluidized bed of the reactor and/or a separator provided downstream of the reactor is at least partly supplied to a cooling system, which comprises in particular an arrangement of a number of cooling stages connected one after the other. In the separator, in particular a cyclone provided downstream of the reactor, the solids (product) discharged with the gas stream passing through the central tube are separated. They are then either supplied directly to a cooling stage for further treatment or returned via a solids return conduit into the annular fluidized bed of the reactor, it also being possible for part of the solids separated in the separator to reach the cooling system and the remaining part to return to the annular fluidized bed. A major advantage of this flexible solids recirculation is that the solids loading of the suspension in the region of the mixing chamber of the reactor can be deliberately adjusted to the requirements of the process and even changed as and when required during operation.

For adjusting the recirculation of the solids, in a development of the idea of the invention it has proven to be advantageous to measure the pressure loss between the central tube and the discharge conduit of the reactor, leading to the separator, and to regulate it by varying the amount of solids recirculated. A flu-

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idized intermediate container with a downstream dosing device, for instance a variable-speed rotary-vane feeder or a roller-type rotary valve, has turned out to be particularly advantageous for this, it being possible for the solids not needed for recirculation to be discharged for example by means of an overflow and
5 passed to the cooling system. The solids recirculation contributes in a simple way to keeping the process conditions constant in the reactor and/or adjusting the mean retention time of the solids in the reactor.

Gentle cooling of the product with a high heat transfer can be achieved in the
10 cooling system if the product to be cooled forms at least in one cooling stage, preferably the last cooling stage of the cooling system, at least one, in particular stationary, fluidized bed, in which it is cooled by a fluidizing gas such as air. Especially in a stationary fluidized bed, a long retention time, and consequently effective cooling, of the product can be achieved by the, for example pre-cooled,
15 fluidizing gas in a comparatively simple manner. Moreover, the mechanical loading of the product is comparatively low in a stationary fluidized bed. If, however, particularly rapid cooling is to take place, a cooling stage with a stationary fluidized bed and a mixing chamber, for instance corresponding to the reactor described above, may also be used. Consequently, the principle ac-
20 cording to the invention of combining a stationary and a circular annular fluidized bed in accordance with the present invention can be used both for heating and cooling fine-grained solids. Cooling occurs when the solids are warmer than the gas stream passing through the central tube, at the beginning of the process. Additional cooling can be achieved by a cooling coil with cooling medium, for
25 example water, formed in particular within the stationary annular fluidized bed.

For improved energy utilization, it is provided that the gas which is used for cooling in a cooling stage, and is thereby heated, is supplied to an upstream cooling stage, the reactor, the combustion chamber and/or a pre-heating stage. It is conceivable to pass the gas through a number of, or all of the preceding cooling
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stages in a cascading manner, beginning with the last cooling stage, in which the product to be cooled has already been pre-cooled by preceding cooling stages. Since the product in the preceding cooling stages is still warmer in each case, it is further cooled in each of the cooling stages and the gas used for the cooling is further heated. Finally, the heated gas can then be supplied to the combustion chamber, the reactor and/or a pre-heating stage.

A plant in accordance with the invention, which is in particular suited for performing the method described above, has a reactor constituting a fluidized bed reactor for the heat treatment of fine-grained solids, in particular gypsum, the reactor having a gas supply system which is formed such that gas flowing through the gas supply system entrains solids from a stationary annular fluidized bed, which at least partly surrounds the gas supply system, into the mixing chamber. Preferably, this gas supply system extends into the mixing chamber. It is, however, also possible to let the gas supply system end below the surface of the annular fluidized bed. The gas is then introduced into the annular fluidized bed for example via lateral apertures, entraining solids from the annular fluidized bed into the mixing chamber due to its flow velocity.

In accordance with the invention, the gas supply system preferably has a central tube extending upwards substantially vertically from the lower region of the reactor, preferably into the mixing chamber of the reactor, which tube is surrounded by a chamber which extends at least partly around the central tube and in which the stationary annular fluidized bed is formed. The central tube may be formed at its outlet opening as a nozzle and/or have one or more distributed apertures in its shell surface, so that during the operation of the reactor solids constantly get into the central tube through the apertures and are entrained by the first gas or gas mixture through the central tube into the mixing chamber. Of course, two or more central tubes with different or identical dimensions and shapes may also be provided in the reactor. Preferably, however, at least one of the central tubes

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is arranged approximately centrally with reference to the cross-sectional area of the reactor.

5 In accordance with a preferred embodiment, a separator, in particular a cyclone, is provided downstream of the reactor, for the separation of solids, the separator having a solids conduit leading to the annular fluidized bed of the reactor and/or a solids conduit leading to the cooling system. In order also to be able to remove the finished product directly from the reactor, a solids conduit leading from the annular fluidized bed to the cooling system is further provided in accordance
10 with the invention.

To provide for a reliable fluidization of the solids and the formation of a stationary fluidized bed, provided in the annular chamber of the reactor is a gas distributor which divides the chamber into an upper annular fluidized bed and a lower
15 gas distributor chamber, the gas distributor chamber being connected to a supply conduit for fluidizing gas. Instead of the gas distributor chamber, a gas distributor composed of tubes and/or nozzles may also be provided.

For adjusting the necessary process temperatures in the reactor, provided
20 upstream of the latter is a combustion chamber with supply conduits for fuel, oxygen and/or heated gas, the exhaust gas of which is passed into the central tube for heating the reactor.

Arranged behind the reactor is a cooling system, comprising direct and/or indirect cooling stages, in particular cooling cyclones and/or fluidized bed coolers.
25 In the case of the direct cooling stages, the cooling medium comes directly into contact with the product to be cooled. In this case, other desired reactions, for example product refinements, can also be carried out during the cooling process. Moreover, the cooling action is particularly good in the case of direct cooling stages. In the case of indirect cooling stages, the cooling takes place by
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means of a cooling medium flowing through a cooling coil. In order to be able also to utilize the gas heated during the cooling in the process itself, a cooling stage has at least one supply conduit leading into a pre-heating stage, into the mixing chamber, into the gas distributor chamber and/or into the combustion chamber.

In the annular fluidized bed and/or the mixing chamber of the reactor, means for deflecting the solids and/or fluid flows may be provided in accordance with the invention. It is for instance possible to position an annular weir, whose diameter lies between that of the central tube and that of the reactor wall, in the annular fluidized bed such that the upper edge of the weir protrudes beyond the solids level obtained during operation, whereas the lower edge of the weir is arranged at a distance from the gas distributor or the like. Thus, solids raining out of the mixing chamber in the vicinity of the reactor wall must first pass by the weir at the lower edge thereof, before they can be entrained by the gas flow of the central tube back into the mixing chamber. In this way, an exchange of solids is enforced in the annular fluidized bed, so that a more uniform retention time of the solids in the annular fluidized bed is obtained.

Developments, advantages and application possibilities of the invention also emerge from the following description of exemplary embodiments and the drawings. All features described and/or illustrated in the drawing form the subject-matter of the invention per se or in any combination, independently of their inclusion in the claims or their back-reference.

Brief Description of the Drawings

Fig. 1 shows a process diagram of a method and a plant in accordance with a first exemplary embodiment of the present invention;

Fig. 2 shows a process diagram of a method and a plant in accordance with a second exemplary embodiment of the present invention.

Detailed Description of the Preferred Embodiments

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The plant and the method for the heat treatment of solids, such as for example gypsum, are firstly described generally on the basis of Fig. 1 to explain the functional principle according to the invention.

10 For the heat treatment, in particular calcining, of solids, the plant has a reactor 1, which is cylindrical for example, with a central tube 3, which is arranged approximately coaxially with the longitudinal axis of the reactor and extends substantially vertically upwards from the bottom of the reactor 1. Provided in the region of the bottom of the reactor 1 is an annular gas distributor 36, into which
15 supply conduits 27 and 37 open out. Arranged in the vertically upper region of the reactor 1, which forms a mixing chamber 21, is a discharge conduit 4, which opens out into a separator 5 formed as a cyclone.

If solids are then introduced into the reactor 1 via the solids conduit 9, a layer
20 annularly surrounding the central tube 3, which is referred to as an annular fluidized bed 2, forms on the gas distributor 36. Both the reactor 1 and the central tube 3 may of course also have a cross section other than the preferred round cross section, as long as the annular fluidized bed 2 at least partly surrounds the central tube 3. Fluidizing gas introduced through the supply conduit 27, 37 flows
25 through the gas distributor 36 and fluidizes the annular fluidized bed 2, so that a stationary fluidized bed is formed. The gas distributor 34 is preferably formed for this purpose as a nozzle grating with a relatively large number of individual nozzles, which are connected to the supply conduits 27, 37. In a more simple embodiment, the gas distributor 36 may also be formed as a grating with a gas
30 distributor chamber located under it. The velocity of the gases supplied to the

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reactor 1 is then adjusted such that the particle Froude number in the annular fluidized bed 2 is approximately 0.3.

By supplying further solids into the annular fluidized bed 2, the level of the solids in the reactor 1 increases to the extent that solids reach the orifice of the central tube 3. At the same time, a hot gas or gas mixture, which is generated in an upstream combustion chamber 26 by burning gaseous, liquid or solid fuels, is introduced into the reactor 1 through the central tube 3. The velocity of the hot gas supplied to the reactor 1 through the central tube 3 is preferably adjusted such that the particle Froude number in the central tube 3 is approximately 10 and in the mixing chamber 21 is approximately 3.0.

Due to banking of the level of the solids of the annular fluidized bed 2 as compared to the upper edge of the central tube 3, solids flow over this edge into the central tube 3. The upper edge of the central tube 3 may be straight or differently shaped, for example indented, or have lateral apertures. Due to the high gas velocities, the gas flowing through the central tube 3 entrains solids from the stationary annular fluidized bed 2 into the mixing chamber 21 when passing through the upper orifice region, whereby an intensively mixed suspension is formed. The intensive mass and heat transfer between the gas stream and the solids in the mixing chamber 21 has the effect that the previously colder solids are heated particularly well by the warmer gas stream and the gas stream is thereby cooled. If the solids are warmer than the gas stream, a cooling of the solids takes place in a way corresponding to the principle according to the invention.

As a result of the reduction of the flow velocity by the expansion of the gas jet in the mixing chamber 21 and/or by impingement on one of the reactor walls, the entrained solids quickly lose speed and partly fall back again into the annular fluidized bed 2. Between the reactor regions of the stationary annular fluidized

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bed 2 and the mixing chamber 21 there is thereby obtained a solids circulation. Due to this solids circulation, the solids to be treated circulate for a particularly long time in the reactor 1, it being possible at the same time to utilize the very good heat transfer in the mixing chamber 21.

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The solids not precipitated from the gas stream above the central tube 3 in the mixing chamber 21 and returned directly into the annular fluidized bed 2 are discharged with the hot gas stream from the reactor 1 upwards through a discharge conduit 4, separated from the gas stream in a separator 5 formed as a cyclone and at least partly returned into the annular fluidized bed 2 through the solids return conduit 6.

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The solids to be treated are thus in total returned into the annular fluidized bed 2 in two ways: after separation from the gas stream in the mixing chamber 21 and after separation in the separator 5 through the solids return conduit 6.

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The heat content of the gas stream leaving the separator 5 is utilized in a multi-stage, in the present case two-stage, system of pre-heating stages 32, 33, which are composed of heat exchangers 40, 10 with downstream separators 12, 8. In this case, the solids to be treated are supplied as raw material to the last heat exchanger 10 on the exhaust gas side, formed as a venturi dryer. There, the supplied solids are suspended in the exhaust gas of the separator 8 of the upstream (second-last) pre-heating stage 32, dried, pre-heated and passed through a solids conduit 11 to the separator 12. The solids separated there are supplied through a solids conduit 13 to the heat exchanger 40 of the second-last pre-heating stage 32, while the exhaust gas escapes. The solids are then suspended by the exhaust gas leaving the separator 5, further pre-heated and supplied through the solids conduit 7 to the separator 8. The pre-heated solids separated there are supplied through the solids conduit 9 to the annular fluidized

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bed 2 of the reactor 1, with the exhaust gas of the separator 8 in turn being passed to the last pre-heating stage 33.

After the heat treatment in the reactor 1, the amount of product, corresponding to the amount of solids to be treated and introduced into the venturi dryer 10, is supplied to a cooling system 34 either directly from the annular fluidized bed 2 through the product supply conduit 14 or from the solids return conduit 6 through the product supply conduit 15. This cooling system 34 comprises an arrangement of direct and/or indirect cooling stages 35, 19 with heat exchangers, for example cooling cyclones or fluidized bed coolers, by which air required in the process is pre-heated and product heat no longer usable in the process is removed. The selection of the type and number of the individual cooling stages 35, 19 or their cooling units depends substantially on the ratio of the amount of air required in the process to the amount of product to be cooled.

In the first cooling stage 35, the product to be cooled is supplied to a rising conduit 16 through the product supply conduits 14, 15. In this rising conduit 16 and the following cooling cyclone 17, the product is cooled, then separated and supplied to a multi-stage fluidized bed cooler 19 through a solids conduit 18. The air required as fluidizing gas for the fluidized bed cooler 19 is supplied to the individual stages of the fluidized bed cooler 19 through an air conduit 20 connected to a blower, is heated there during the cooling of the product and is passed through the rising conduit 16 to the cooling cyclone 17. In the rising conduit 16, this fluidizing air is further heated, with the product being cooled. Here, the heated air of the second cooling stage 19 is thus passed to the first cooling stage 35. After the dedusting in the cyclone 17, the heated air (fluidizing air) is either directed through supply conduit 22 into the reactor 1 or through supply conduit 41 into the heat exchanger 40 formed as a venturi pre-heater.

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In the multi-stage fluidized bed cooler 19, the product is firstly cooled in one or more stages in counter-current to the combustion air, both indirect cooling taking place through the air conduit 23 and a cooling coil 24, formed as a heat exchanger element, and direct cooling taking place through the air conduit 20 and the fluidizing air fed into the individual stages as a result. The air heated during the indirect cooling is supplied through the supply conduit 25 to the combustion chamber 26 and optionally also through the supply conduit 27 to the annular fluidized bed as fluidizing gas. In the combustion chamber 26, fuel supplied via the fuel conduit 42 is burned with the heated air from the cooling stages and possibly additional air supplied via the air supply 28. The exhaust gas of the combustion chamber is passed through the gas stream conduit 29 to the central tube 3 and as the first gas or gas mixture into the mixing chamber 21.

The product is cooled indirectly in the fluidized bed cooler 19 in one or more stages in counter-current to a cooling medium, for example water, flowing through a cooling coil 31, and directly by the fluidizing air in the individual stages, until the desired end temperature is reached. The cooling medium is passed to the cooling coil 31 via conduit 30 and subsequently removed again via conduit 45.

A particular advantage of this method is that the advantages of a stationary fluidized bed (annular fluidized bed) and a circulating fluidized bed in a mixing chamber can be optimally utilized and at the same time the waste heat produced by the cooling of the product is supplied again to the reactor to save energy.

Example (calcining of gypsum)

The calcining of REA gypsum to form water-free anhydrite is described in detail below on the basis of Fig. 2, which shows a plant similar to Fig. 1. Moist gypsum is introduced into the venturi dryer 10 by means of the screw conveyor 38

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with a volumetric flow of for example 42 t/h from a storage bunker 39 and suspended by exhaust gas from the cyclone 8, dried and supplied to a separator 12, formed as a cyclone, via the solids conduit 11. The exhaust gas from the cyclone 12 is passed to a bag filter 43, where it is freed completely of solids and
5 blown out by an exhaust gas blower 44 via a stack.

The dried gypsum separated in the cyclone 12 and the bag filter 43 is passed via solids conduits 13 to a second venturi dryer 40, heated further, separated from the exhaust gas in the cyclone 8 and introduced into the fluidized bed 2 of the reactor 1 through the solids conduit 9. In the combustion chamber 26, about
10 36,000 Nm³/h of hot gas with a temperature of about 1,130°C are generated and passed to the reactor 1 through the gas-stream conduit 29. The hot gas cools in the reactor 1 to about 750°C. At the same time, the gypsum introduced into the reactor, which has a grain size of less than 0.2 mm, is heated to about 750°C
15 and calcined to form anhydrite. The solids are transported with the exhaust gases of the reactor 1 into the return cyclone 5 (separator), separated there and largely returned through the solids return conduit 6 into the annular fluidized bed 2 of the reactor 1.

20 The part-stream of the amount of anhydrite product, which corresponds to the amount of gypsum introduced into the reactor 1, is supplied through the product supply conduit 15 to the rising conduit 16 belonging to the cooling cyclone 17 of the first cooling stage 35. The anhydrite is cooled in the cooling cyclone 17 to about 600°C and passed through the solids conduit 18 to a first chamber of the
25 fluidized bed cooler 19. The exhaust air of the cooling cyclone 17 is passed through the supply conduit 41 to the venturi dryer 40.

In the fluidized bed cooler 19, the anhydrite is cooled in stages to about 80°C. The amount of product is about 30 t/h. During the cooling of the anhydrite, the
30 burner air (about 14,000 Nm³/h) supplied through the air conduit 23 is indirectly

heated to about 450°C in banks of heat exchangers which are formed as cooling coils 24 and are installed in the first two chambers of the fluidized bed cooler 19. This air is supplied to the combustion chamber 26 through the supply conduit 25. As fuel, about 1,300 Nm³/h of natural gas are supplied to the combustion chamber 26 through the fuel conduit 42. In addition, further combustion air (about 21,000 Nm³/h) is blown into the combustion chamber through the air supply 28. The amount of fuel and the amount of combustion air are adjusted such that a hot-gas temperature of about 1,130°C and the desired reactor temperature of about 750°C are reached at the outlet of the combustion chamber 26.

The end cooling of the anhydrite takes place in the last two chambers of the fluidized bed cooler 19. Cooling water is supplied through the conduit 30 to the banks of cooling tubes installed in two chambers as cooling coil 31 and returned through the conduit 45. The required fluidizing air is supplied to the fluidized bed cooler 19 through the conduit 20.

List of Designations:

1	reactor	24	cooling coil
2	annular fluidized bed	25	supply conduit
3	central tube	26	combustion chamber
4	discharge conduit	27	supply conduit
5	separator	28	air supply
6	solids return conduit	29	gas-stream conduit
7	solids conduit	30	conduit
8	separator	31	cooling coil
9	solids conduit	32	pre-heating stage
10	heat exchanger	33	pre-heating stage
11	solids conduit	34	cooling system
12	separator	35	cooling stage
13	solids conduit	36	gas distributor
14	product supply conduit	37	supply conduit
15	product supply conduit	38	screw conveyor
16	rising conduit	39	storage bunker
17	cooling cyclone	40	heat exchanger
18	solids conduit	41	supply conduit
19	cooling stage, fluidized bed cooler	42	fuel conduit
		43	bag filter
20	air conduit	44	exhaust gas blower
21	mixing chamber	45	conduit
22	supply conduit		
23	air conduit		

Claims:

1. A method for the heat treatment of fine-grained solids, in particular gypsum, in which the solids are heated to a temperature of 50 to 1000°C in a fluidized bed reactor (1), characterized in that a first gas or gas mixture is introduced from below through a preferably central gas supply tube (3) into a mixing chamber (21) of the reactor (1), the gas supply tube (3) being at least partly surrounded by a stationary annular fluidized bed (2) which is fluidized by supplying fluidizing gas, and in that the gas velocities of the first gas or gas mixture as well as of the fluidizing gas for the annular fluidized bed (2) are adjusted such that the particle Froude numbers in the gas supply tube (3) are between 1 and 100, in the annular fluidized bed (2) between 0.02 and 2 and in the mixing chamber (21) between 0.3 and 30.

2. The method as claimed in claim 1, characterized in that the particle Froude number in the gas supply tube (3) is between 1.15 and 20.

3. The method as claimed in claim 1 or 2, characterized in that the particle Froude number in the annular fluidized bed (2) is between 0.115 and 1.15.

4. The method as claimed in any of the preceding claims, characterized in that the particle Froude number in the mixing chamber (21) is between 0.37 and 3.7.

5. The method as claimed in any of the preceding claims, characterized in that the bed height of the solids in the reactor (1) is adjusted such that the annular fluidized bed (2) extends beyond the upper orifice end of the gas supply tube (3), and that solids are constantly introduced into the first gas or gas mixture and entrained by the gas stream to the mixing chamber (21) located above the orifice region of the gas supply tube (3).

6. The method as claimed in any of the preceding claims, characterized in that fine-grained solids, for example moist gypsum, with a grain size of less than 2 mm, in particular less than 0.2 mm, are supplied as the starting material.

5

7. The method as claimed in any of the preceding claims, characterized in that hot gas, which is generated in an upstream combustion chamber (26) by burning supplied fuel, possibly with the admixture of a gas containing oxygen, is supplied to the reactor (1) via the gas supply tube (3).

10

8. The method as claimed in any of the preceding claims, characterized in that the solids are heated in the reactor (1) to a temperature of 150 to 1000°C.

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9. The method as claimed in any of the preceding claims, characterized in that air is supplied to the reactor (1) as fluidizing gas.

10. The method as claimed in any of the preceding claims, characterized in that the pressure in the reactor (1) is between 0.8 and 10 bar.

20

11. The method as claimed in any of the preceding claims, characterized in that, before the heat treatment in the reactor (1), the solids are suspended, dried and/or pre-heated in at least one pre-heating stage (32, 33), comprising a heat exchanger (6, 10) and a downstream separator (8, 12).

25

12. The method as claimed in any of the preceding claims, characterized in that, after the heat treatment in the reactor (1), the product from the annular fluidized bed (2) of the reactor (1) and/or a separator (5) provided downstream of the reactor (1) is at least partly supplied to a cooling system (34), which comprises in particular an arrangement of a number of cooling stages (35, 19) connected one after the other.

30

13. The method as claimed in claim 12, characterized in that the product forms in a cooling stage (19) at least one fluidized bed, in which it is cooled by a fluidizing gas, in particular air, and/or a cooling coil (24, 31), formed in the fluidized bed, with cooling medium, in particular water.

14. The method as claimed in claim 12 or 13, characterized in that the gas heated in a cooling stage (19, 17) is supplied to an upstream cooling stage (17), the reactor (1), the combustion chamber (26) and/or a pre-heating stage (32).

15. A plant for the heat treatment of fine-grained solids, in particular for performing a method as claimed in any of claims 1 to 13, comprising a reactor (1) constituting a fluidized bed reactor for the heat treatment, characterized in that the reactor (1) has a gas supply system which is formed such that gas flowing through the gas supply system entrains solids from a stationary annular fluidized bed (2), which at least partly surrounds the gas supply system, into the mixing chamber (21).

16. The plant as claimed in claim 15, characterized in that the gas supply system has a gas supply tube (3) extending upwards substantially vertically from the lower region of the reactor (1) into the mixing chamber (21) of the reactor (1), the gas supply tube (3) being surrounded by a chamber which extends at least partly around the gas supply tube and in which a stationary annular fluidized bed (2) is formed.

17. The plant as claimed in claim 15 or 16, characterized in that the gas supply tube (3) is arranged approximately centrally with reference to the cross-sectional area of the reactor (1).

– 23 –

18. The plant as claimed in any of claims 15 to 17, characterized in that a separator (5) is provided downstream of the reactor (1), for the separation of solids, and that the separator (5) has a solids conduit (6) leading to the annular fluidized bed (2) of the reactor (1) and/or a solids conduit (15) leading to the cooling system (34).

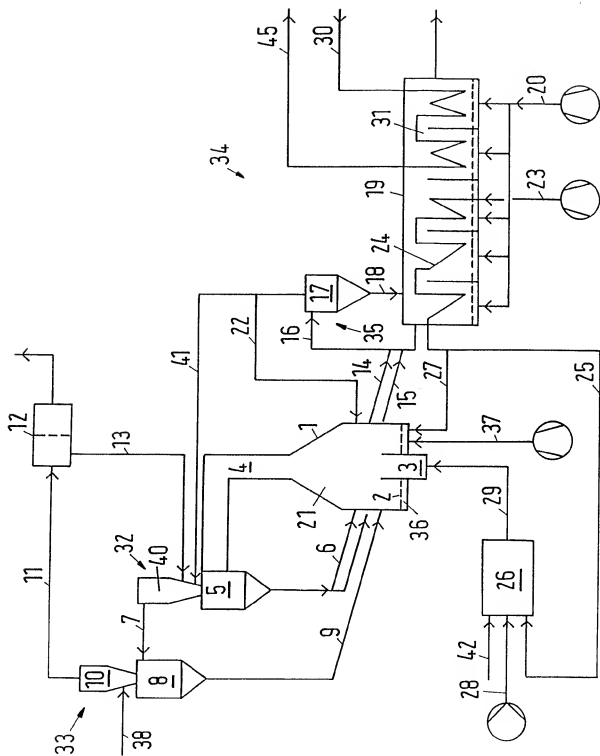
19. The plant as claimed in any of claims 15 to 18, characterized in that a solids conduit (14) leading from the annular fluidized bed (2) of the reactor (1) to the cooling system (34) is provided.

20. The plant as claimed in any of claims 15 to 19, characterized in that, provided in the annular chamber of the reactor (1) is a gas distributor (36) which divides the chamber into an upper annular fluidized bed (2) and a lower gas distributor (36), and that the gas distributor (36) is connected to a supply conduit (37, 27) for fluidizing gas.

21. The plant as claimed in any of claims 15 to 20, characterized in that, provided upstream of the reactor (1) is a combustion chamber (26) with supply conduits (42, 28, 25) for fuel, oxygen and/or heated gas, the exhaust gas of which is passed into the gas supply tube (3).

22. The plant as claimed in any of claims 15 to 21, characterized in that, provided downstream of the reactor (1) is a cooling system (34), comprising direct and/or indirect cooling stages (35, 19), in particular cooling cyclones and/or fluidized bed coolers.

Fig.1



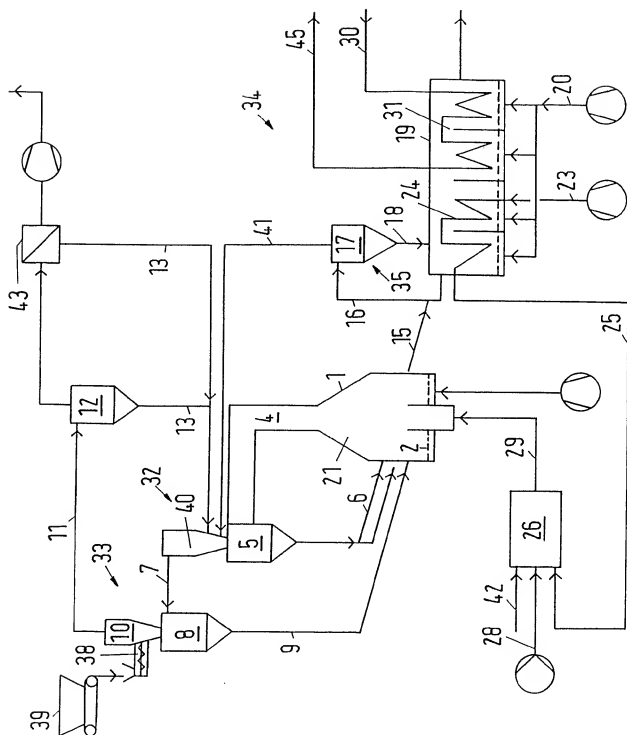


Fig. 2

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP 03/13982A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J8/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 630 683 A (AHLSTROEM OY) 28 December 1994 (1994-12-28)	15-22
A	abstract; figure 1	1-14
A	US 6 015 539 A (SCHMIDT HANS WERNER ET AL) 18 January 2000 (2000-01-18)	1-22
A	abstract; figure 1	
A	US 4 817 563 A (KNOCH RONALD ET AL) 4 April 1989 (1989-04-04)	1-22
	abstract; figure 3	

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP 03/13982

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0630683	A	28-12-1994	FI 93274 B 30-11-1994
			AT 176604 T 15-02-1999
			AT 177661 T 15-04-1999
			DE 69416458 D1 25-03-1999
			DE 69416458 T2 02-09-1999
			DE 69417103 D1 22-04-1999
			DE 69417103 T2 16-09-1999
			EP 0630683 A1 28-12-1994
			EP 0630684 A1 28-12-1994
			FI 941543 A ,B, 24-12-1994
			JP 7136493 A 30-05-1995
			JP 7136494 A 30-05-1995
			US 5505907 A 09-04-1996
			US 5634516 A 03-06-1997
US 6015539	A	18-01-2000	DE 19542309 A1 15-05-1997
			AT 209607 T 15-12-2001
			AU 728011 B2 04-01-2001
			AU 7497096 A 05-06-1997
			BR 9611386 A 24-10-2000
			CA 2235706 A1 22-05-1997
			CN 1204302 A ,B 06-01-1999
			DE 59608329 D1 10-01-2002
			DK 861208 T3 25-03-2002
			EA 980451 A1 29-10-1998
			WO 9718165 A1 22-05-1997
			EP 0861208 A1 02-09-1998
			ES 2169270 T3 01-07-2002
			ID 17589 A 15-01-1998
			IN 186958 A1 22-12-2001
			JP 2000512255 T 19-09-2000
US 4817563	A	04-04-1989	SK 64298 A3 12-07-1999
			DE 3706538 A1 08-09-1988
			AT 68577 T 15-11-1991
			AU 589108 B2 28-09-1989
			AU 1234088 A 01-09-1988
			CA 1324881 C 07-12-1993
			DD 269430 A5 28-06-1989
			DE 3865460 D1 21-11-1991
			EP 0281165 A1 07-09-1988
			ES 2026631 T3 01-05-1992
			FI 880717 A ,B, 29-08-1988
			GR 3002903 T3 25-01-1993
			IN 165700 A1 16-12-1989
			JP 2564163 B2 18-12-1996
			JP 63233204 A 28-09-1988
			ZA 8801385 A 25-10-1989